

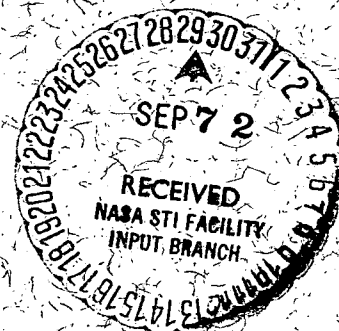
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NASA TM X-66024

THE DISTRIBUTION OF NO₂⁺ IN THE LOWER IONOSPHERE

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SEPTEMBER 1972



GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

(NASA-TM-X-66024) THE DISTRIBUTION OF
NO₂(PLUS) IN THE LOWER IONOSPHERE A.C.
Aiken, et al (NASA) Sep. 1972 10 p CSCL

N72-32395

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THE DISTRIBUTION OF NO_2^+ IN THE LOWER IONOSPHERE

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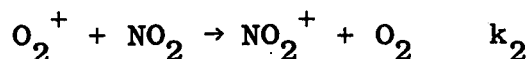
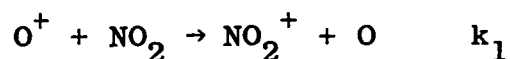
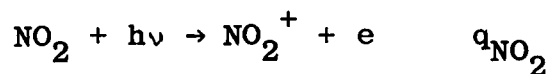
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The ion NO_2^+ (46 AMU) has been observed as a minor ionic constituent of the lower ionosphere. Data were obtained by means of a quadrupole ion mass spectrometer, similar to that described by Goldberg and Aikin (1971). The spectrometer was flown on rocket NASA 14.167 from Keweenaw, Michigan (Lat. 47.4°N , Long. 87.8°W) on January 29, 1971 at a solar zenith angle, χ , of 67° . An example of a mass scan near 90 km is presented in Figure 1. The ion 46^+ is most prevalent in the vicinity of 90 km and is always observed in the presence of 48^+ , which is identified as $\text{NO}^+\cdot\text{H}_2\text{O}$. It has also been detected with similar features in a midlatitude summer ionosphere at El Arenosillo, Spain (Lat. 37.1°N , Long. 6.7°W) for $\chi = 57^\circ$, although with less enhancement. Table I presents the ratio of $48^+/46^+$ as a function of altitude for Keweenaw, Michigan, together with concentrations of $\text{O}^+(16^+)$, $\text{O}_2^+(32^+)$, 46^+ , 48^+ and the electron density N_e , which was obtained by the Faraday rotation radio propagation technique. For comparison the ratio at 91 km for El Arenosillo is 6.6. The values of the low density constituents

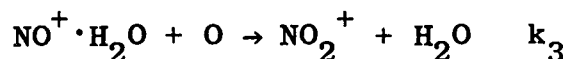
are believed to be correct to a factor of 2; O_2^+ is accurate to $\pm 20\%$.

The only other measurement of the ion 46^+ , also in the presence of 48^+ , was reported by Narcisi (1969). However, this measurement occurred from Ft. Churchill at sunset during a period of enhanced ionization.

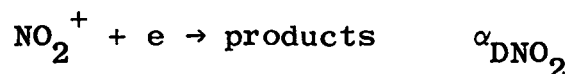
Several reactions govern the distribution of NO_2^+ . Most important are



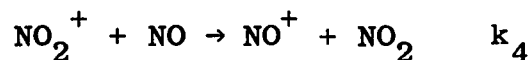
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Loss processes include



and



The laboratory coefficients for the reactions are:

$$k_1 = 1.6(-9) \text{ cm}^3 \text{ sec}^{-1} \text{ (Dunkin et al, 1971) and}$$

$$k_4 = 2.9(-10) \text{ cm}^3 \text{ sec}^{-1} \text{ (Fehsenfeld et al, 1969). } k_2 \text{ and}$$

α_{DNO_2} have not been measured. It is assumed that $k_2 = k_1$ and that $\alpha_{DNO_2} = 4 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$.

Photoionization studies of NO_2 yield 9.75 eV for the NO ionization potential (Diebler et al, 1967). This allows mesospheric NO_2 to be ionized by radiation of wavelength

shorter than 1240 Å including solar Lyman alpha at 1216 Å.

The ion pair production function can be written as

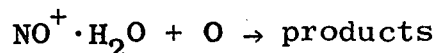
$q_{\text{NO}_2} = 0.05([\text{NO}_2]/[\text{NO}]) q_{\text{NO}} \text{ cm}^{-3} \text{ sec}^{-1}$, where .05 is the ratio of the ionization cross sections of NO_2 and NO at Lyman alpha (Nakayama et al, 1959). The ratio $[\text{NO}_2]/[\text{NO}]$ has been derived by Nicolet (1965) and his value at 90 km is given in Table II together with the resultant q_{NO_2} for the nitric oxide concentrations of Meira (1971).

The equilibrium concentration of NO_2^+ can be calculated from the relation

$$[\text{NO}_2^+] = \frac{q_{\text{NO}_2} + k_1[\text{O}^+][\text{NO}_2] + k_2[\text{O}_2^+][\text{NO}_2] + k_3[\text{NO}^+\cdot\text{H}_2\text{O}][\text{O}]}{\alpha_{\text{DNO}_2} N_e + k_4[\text{NO}]}$$

At 90 km, photoionization and charge exchange between O^+ , O_2^+ and NO_2 account for 1.5×10^{-2} , 2.7×10^{-3} and 2.3×10^{-1} ions cm^{-3} , respectively. On the other hand, if the reaction rate k_4 has a rate coefficient of $3 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$, the calculation yields a value of 8 ions cm^{-3} for the concentration of NO_2^+ .

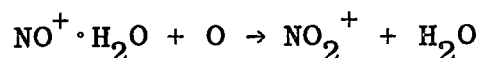
Heimerl (private communication) has derived an upper limit for



of $5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ in order to avoid breaking the chain which transforms NO^+ into the water cluster ions observed in the D region. The rate derived here is consistent with that value. The reaction has not been measured in the laboratory and will probably prove difficult if the rate coefficient is as small as predicted here.

It might be expected that the hydrate of NO_2^+ would be detected. On one occasion 64^+ was observed, but it is not clear if this was $\text{NO}_2^+ \cdot \text{H}_2\text{O}$ or O_4^+ , which is also expected to be a minor component of the D region ion population.

In summary, photoionization and charge exchange reactions appear to be insufficient to account for the observed concentration of NO_2^+ at 90 km. The reaction



is a possible alternate. Use of this process as the main source for NO_2^+ is consistent with the observed correlation between NO_2^+ and $\text{NO}^+ \cdot \text{H}_2\text{O}$ as well as the enhancement of NO_2^+ near 90 km, where $[\text{O}]$ is large.

TABLE I
Observed Concentrations of Ions and Electrons

| ALT. (km) | $O^+(16^+)$ | | $O_2^+(32^+)$ | | $NO_2^+(46^+)$ | | $NO^+ \cdot H_2O(48^+)$ | | N_e | $48^+/46^+$ |
|--------------|-------------|-----|---------------|-----|----------------|------|-------------------------|------|-------|-------------|
| | I | II | I | II | I | II | I | II | | |
| 87.8 | -- | -- | 160 | 340 | 3 | 6.3 | 7 | 15.0 | 0.97 | 2.4 |
| 89.2 | 2 | 4.9 | 150 | 340 | 5 | 11.0 | 19 | 44.0 | 1.01 | 4.0 |
| 90.6 | 2.5 | 7.0 | 220 | 620 | 8 | 22.0 | 21 | 58.0 | 1.16 | 2.6 |
| 91.6 | 2 | 4.9 | 120 | 340 | -- | -- | 4 | 11.0 | 1.86 | -- |
| 93.2 | -- | -- | 140 | 500 | 2 | 7.8 | 2 | 7.8 | 2.38 | 1.0 |

Note: Column I - Ion density (cm^{-3})
 II - Ion current (amps) $\times 10^{12}$
 N_e - Electron density (cm^{-3}) $\times 10^{-4}$

TABLE II

Parameters used in computation. Units of q_{NO_2} are $\text{cm}^{-3}\text{sec}^{-1}$ and concentrations, cm^{-3} .

| ALT | q_{NO_2} | N_e | $[\text{NO}_2]/[\text{NO}]$ | $[\text{O}]$ | $[\text{NO}]$ |
|-----|-------------------|--------|-----------------------------|--------------|---------------|
| 90 | 2(-4) | 1.2(4) | 3(-4) | 1.7(11) | 3(7) |

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FIGURE CAPTION

Figure 1 - A typical mass scan obtained aboard NASA 14.167 with a quadrupole ion mass spectrometer. The display is approximately logarithmic in current.

NASA 14.167
 JAN. 29, 1971, X=67°
 KEWEENAW, MICHIGAN

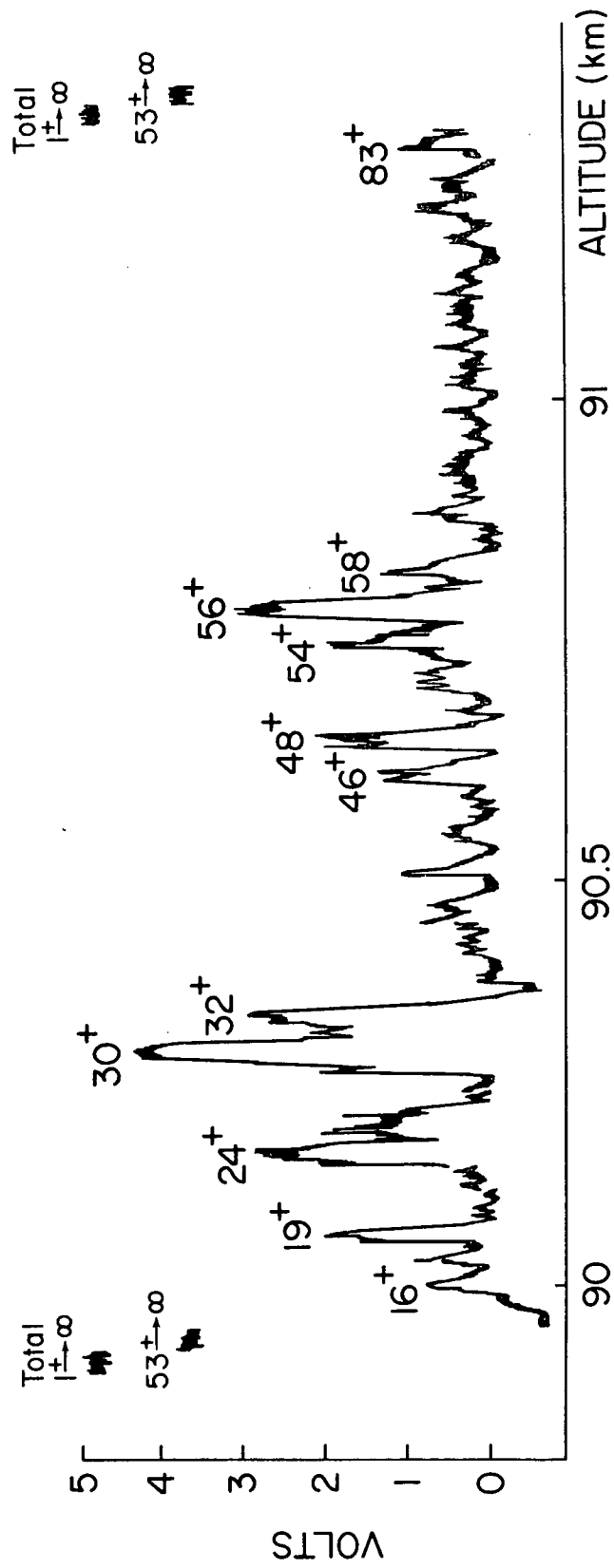


Figure 1